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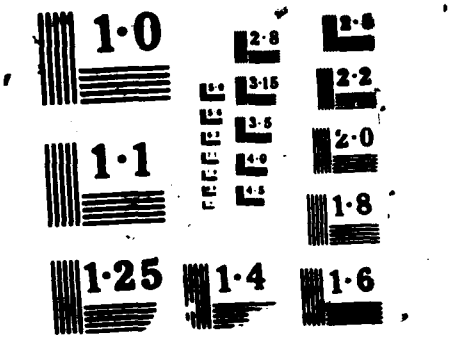
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SCHOTTKY BARRIER PHOTOELECTRODES WITH A VARIABLE BARRIER HEIGHT

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19 ABSTRACT (*Continue on reverse if necessary and identify by block number*)

This program has dealt with characterizing junctions formed between semiconductors and "insertion compounds." Examples of the latter are H_xWO_3 and H_xIrO_2, which have a variable work function according to the stoichiometry parameter, x. Specific applications of the structures to optically activated light modulators and to chemical sensors have been demonstrated.

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SUMMARY

Semiconductor-metal contacts are of fundamental importance in electronics and electro-optical technologies. Typically such contacts are either rectifying or ohmic, depending on the relative work functions of semiconductor and contacting metal, and on the energetic distribution and densities of charge trapping impurities and defects at the interface. Certain non-stoichiometric insertion compounds, like the "bronzes" (M_xWO_3, M_xMoO_3, $M_xV_2O_5$, M = H, Li, Na, Ag), have a work function which varies with x. We demonstrated for the first time junctions between a variable work function insertion compound, M_xWO_3, and several semiconductors, and showed that the barrier height could be adjusted by adjusting the value of x. Junctions between H_xWO_3 and n-Si were varied between ohmic (x=0.4) and rectifying with a barrier height of approximately 0.3 ev (x=0.1). It was also demonstrated that the photovoltage of H_xWO_3/n or p-Si or n-CdS could also be varied by changing x, in a manner predictable from their solid state properties. These basic results led to our demonstrating two new devices based on these junctions: chemical sensors and self-adjusting "photovoltaic light modulators".

A variety of imaging devices were developed based on the fact that the optical absorption of the "bronzes" generally increases with increasing x (the electrochromic effect, if M is inserted electrochemically). An example of the photovoltaic element is H_xWO_3/p-Si. We have been investigating independently electrochromic light modulators of the following configuration:

$$\text{Glass}|\text{ITO}|H_xWO_3|H^+ \text{ conductor}|IrO_2|\text{ITO}|\text{Glass}$$

where ITO is a transparent, electronically conductive thin oxide film and the H^+ conductor is the transparent solid polymeric acid, "polyAMPs". When electrical current is applied between the two ITO layers such that H_xWO_3 becomes the anode, H is electrolytically transferred to the IrO_2. Since both WO_3 and H_xIrO_2 are colorless, and since both H_xWO_3 and IrO_2 are deeply colored, the structure may thus be switched between absorbing and transparent states ($\sim$10 mC/cm^2 is required at $\sim$1V). When one of the ITO|glass layers is replaced by a semiconductor, the structure becomes a photoelectrolytic light modulator. Thus, in the case of p-Si|WO_3, illumination produces minority carrier electrons in the p-Si which will result in reductive insertion of H into the WO_3 layer and a coloration of the device if the two ITO layers are connected. As x increases, so does the barrier height, which automatically compensates for the additional voltage required to drive the "electrochromic battery" to an increasing state of charge. When the p-Si is partially mirrored, then a variable reflector results whose reflectance is proportional to the ambient light level.

A new class of chemical sensors was demonstrated based on insertion compounds, and a patent application filed. The sensitive component of the solid state structures is a bilayer consisting of 20-100A of a catalytic metal on the surface of an amorphous WO_3 thin film ($\sim$2000A). The catalytic metal is

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chosen to yield decomposition products which spontaneously insert into the WO_3 and change both its work function and electrical resistivity. This bilayer can then be incorporated into a variety of metal-oxide-semiconductor, metal-semiconductor and metal-oxide-metal diode structures and the chemical response detected as resistance or capacitance. For example, a H_2 sensor was fabricated by employing Pd as the catalyst. The negative free energy associated with the transfer of H atoms from Pd to the WO_3 permits the device to operate smoothly at room temperature, unlike previously existing solid state H_2 sensors. Furthermore, devices with Pt appear to be more sensitive to higher hydrocarbons and alcohols when the WO_3 is present to supply this extra thermodynamic boost. The high mobility of H^+ in the amorphous WO_3 further ensures a very rapid response and little baseline drift.

The "xerogel" nature of the thin film oxides prepared at low temperature also makes them susceptible to exchange reactions, much like silica gels. The adsorption of H_2O into the internal pore structure of the films can readily be detected by ac methods as a change in dielectric constant and ion conductivity. Thus, a new series of humidity sensors was demonstrated with an unusually wide dynamic range.

A matrix of sensitivities of some of the devices developed on this program is provided in Table 1.

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Reports: Internal technical progress reports were submitted quarterly to the Scientific Officer, ONR.

Publications and Presentations:

Properties of Schottky Diodes using H_xWO_3 as a Variable Work Function Metal, T.L. Rose, S.N. Benoit and R.D. Rauh, Paper 55, Fall Meeting of the Electrochemical Society, Las Vegas, 1985.

Semiconductor/H_xWO_3 Interfaces: Properties and Applications, R.D. Rauh, T.L. Rose, S.N. Benoit and T.D. Plante, Paper 612, Fall Meeting of the Electrochemical Society, San Diego, 1986.

Variable Barrier Height Semiconductor/H_xWO_3 Diodes, R.D. Rauh T.L. Rose and S.N. Benoit, Appl. Phys. Lett. 48, 362 (1986).

TABLE 1

SENSITIVITIES OF MOS INSERTION SENSORS TO VARIOUS GASES

Structure	T(°C)	5% H_2O	5% H_2	(Sat. 25°) CH_3OH	(Sat. 25°) C_2H_5OH	(2000 ppm) CO
p-Si/SiO_2 (500Å)/WO_3 (3000Å)/Pt (200Å)	25	+	+	+	+	-
	150	-	+	+	+	-
p-Si/SiO_2 (500Å)/WO_3 (3000Å)/Pt (200Å)	25	+	+	+	+	-
	150	-	+	+	-	-
p-Si/SiO_2 (500Å)/WO_3 (3000Å)/Au (200Å)	25	+	-	-	+	-
	150	-	+	+	-	-
n-Si/SiO_2 (500Å)/WO_3 (3000Å)/Pt (200Å)	25	N/A	+	+	+	-
	150	N/A	+	+	+	-
n-Si/SiO_2 (500Å)/WO_3 (3000Å)/Pd (200Å)	25	N/A	+	+	N/A	N/A
	150	N/A	+	+	N/A	N/A
n-Si/SiO_2 (500Å)/WO_3 (3000Å)/Au (200Å)	25	+	-	+	N/A	N/A
	150	-	+	-	N/A	N/A
p-Si/SiO_2 (500Å)/Pt (200Å)	25	-	+	-	-	-
	150	-	+	+	-	-
p-Si/SiO_2 (500Å)/Pd (200Å)	25	-	+	-	-	-
	150	-	+	-	-	-
p-Si/SiO_2 (500Å)/Au (200Å)	25	-	-	-	-	-
	150	-	-	-	-	-
n-Si/SiO_2 (500Å)/Pt (200Å)	25	N/A	+	+	-	-
	150	N/A	+	+	+	-
n-Si/SiO_2 (500Å)/Pd (200Å)	25	N/A	+	-	-	-
	150	N/A	+	-	-	-
n-Si/SiO_2 (500Å)/Au (200Å)	25	N/A	-	-	-	-
	150	N/A	-	-	-	-

Patent Filed: Chemical Sensor, U.S. Patent Appl. No. 894,285, August 7, 1986 (R. David Rauh).

Invited Presentation: Chemical Insertion Sensors, Plenary Lecture, 6th International Conference on Solid State Ionics, Garmisch-Partenkirchen, Federal Republic of Germany, Sept. 6-11, 1987.

Chemical Sensitivity of $Si|WO_3$ and $Si|SiO_2|WO_3$ Diode Structures, R. David Rauh, Timothy L. Rose and Stephen N. Benoit, Appl. Phys. Letters, to be submitted.

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